

The structure of crichtonite and its relationship to senaite

IAN E. GREY

CSIRO Division of Mineral Chemistry, P. O. Box 124
Port Melbourne, Victoria 3207, Australia

DOUGLAS J. LLOYD

State College of Victoria at Bendigo, Osborne St.
Bendigo, Victoria 3350, Australia

AND JOHN S. WHITE, JR.

Smithsonian Institution, Washington, D.C. 20560

Abstract

Crichtonite, from the Dauphiné region of France, crystallizes in the rhombohedral space group $R\bar{3}$ with lattice parameters $a = 9.148(2) \text{ \AA}$, $c = 69.078(6)$. Its formula, determined from microprobe analysis, is $\text{Sr}_{0.71}(\text{RE}, \text{Pb})_{0.19}\text{Ti}_{13.43}\text{Fe}_{6.71}\text{Mn}_{0.69}(\text{V}, \text{Cr})_{0.17}\text{O}_{38}$. The structure was solved using 505 symmetry-independent reflections collected on a Philips PW 1100 diffractometer with $\text{MoK}\alpha$ radiation and refined to an R value (for all measured data and using isotropic thermal parameters) of 0.040. Crichtonite is isostructural with senaite, with a structure based on a nine-layer (hhc —) close-packed anion lattice in which Sr (and Pb + RE) atoms are ordered in one-thirteenth of the anion sites in the cubic layers. The remaining metals are ordered into one-half of the octahedral sites and one thirty-ninth of the tetrahedral sites, and the polyhedra articulate by edge and corner-sharing only. Both senaite and crichtonite are described by the general formula $(\text{Pb}, \text{Sr})_{1-x}\text{M}_{21}\text{O}_{38}$, and it is proposed that the mineral names apply to the lead- and strontium-dominant compositions, respectively. Senaite containing only divalent iron has the reported composition $\text{PbM}_{24}\text{O}_{38}$, and a structural model has been proposed, based on the senaite/crichtonite structure in $R\bar{3}$, with the three extra metal atoms occupying face-shared octahedral sites, forming segments of ilmenite structure.

Introduction

Although the mineral crichtonite was discovered nearly 190 years ago by J. L. de Bournon, very little information is available on its chemical composition and structure. The only reported quantitative analysis is by Hey *et al.* (1969) who analyzed for ferrous and ferric iron and titanium. The oxides of these elements accounted for 95 weight percent of the sample, and the remainder was considered to be quartz. The analytical data were consistent with a formula $\text{Fe}_{16}^{2+}\text{Fe}_{14}^{3+}\text{Ti}_{66}\text{O}_{169}$. Their single-crystal X-ray studies showed that crichtonite has a prominent rhombohedral pseudo-cell with $a_{\text{hex}} = 2.880 \text{ \AA}$ and $c_{\text{hex}} = 20.759 \text{ \AA}$. They suggested that the true rhombohedral cell had $a_{\text{hex}} = 37.44 \text{ \AA}$, but were unable to completely index their patterns, even

with this cell. Rouse and Peacor (1968) reported (from A. Pabst, private communication) that the 37.44 \AA axis for crichtonite may be given as $10.38 \sqrt{13}$, corresponding to the pseudo- a of twinned davidite, *i.e.* implying that the true cell for *untwinned* crichtonite is rhombohedral with $a_{\text{hex}} = 10.38 \text{ \AA}$, $c_{\text{hex}} = 20.759 \text{ \AA}$. For comparison, the mineral davidite has $a = 10.37 \text{ \AA}$, $c = 20.87 \text{ \AA}$ (Pabst, 1961), and senaite has $a = 10.393 \text{ \AA}$, $c = 20.811 \text{ \AA}$ (Grey and Lloyd, 1976). Strunz (1970, p. 187) has grouped these three minerals together on the basis of their similar compositions and morphologies. We have reported the results of a structure determination on senaite which has the general composition $\text{Pb}_{1-x}(\text{Mn}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti})_{21}\text{O}_{38}$ (Grey and Lloyd, 1976). In a continuing study on the structural relations between

senaitite, davidite, and crichtonite, we studied a crichtonite sample from Dauphiné, France. Microprobe analyses on the samples were consistent with a chemical formula similar to the one given above for senaitite, except that the lead was largely replaced by strontium. We report here a single crystal structure determination for crichtonite and describe the structural and compositional relationships between senaitite and crichtonite.

Experimental

A sample of crichtonite from the Smithsonian Institution collection (U.S.N.M. B18195) was supplied by John S. White, Jr. The specimen, from the Dauphiné region of France, was a large double-crystal implanted on quartz. The results of microprobe analysis are given in Table 1a. The results for the major elements are very similar to those for senaitite (Grey and Lloyd, 1976). The main differences are a greatly reduced lead content for crichtonite and a concomitant increase in the strontium content, compared with the senaitite values, which are included in Table 1.¹ The derived chemical formula, corrected to 38 oxygens, is $\text{Sr}_{0.71}(\text{RE}, \text{Pb})_{0.19} \text{Ti}_{13.43} \text{Fe}_{6.71} \text{Mn}_{0.69}(\text{V}, \text{Cr})_{0.17} \text{O}_{38}$. The ferrous/ferric iron ratio was calculated indirectly from the microprobe data using the criteria from the structure solution that the small cations fully occupied 21 sites in the unit cell and that 38 of the available 39 anion sites were occupied by oxygen, *i.e.* $(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Ti} + \text{Mn} + \text{minor small cations})/\text{O} = 21/38$.

For the initial X-ray diffraction examination a section was cut from one crystal of the double crystal. The crystal was examined using conventional Weissenberg and precession techniques, and our observations were identical with those reported by Hey *et al.* (1969), *i.e.* a rhombohedral cell with $a_{\text{hex}} = 37.4 \text{ \AA}$, $c_{\text{hex}} = 20.7 \text{ \AA}$. A precession photograph of the $(hki0)$ section was the same as that published for twinned davidite by Pabst (1961).

The "twinned" crichtonite crystal was then fragmented, and a resulting thin sliver, 0.25 mm long by 0.075 mm average diameter, was mounted on the precession camera. The fragment was found to be free of twinning and had a unit cell and space group similar to that for senaitite (Grey and Lloyd, 1976) and davidite (Pabst, 1961), *i.e.* trigonal $R\bar{3}$ or $R3$, with hexagonal dimensions $a_{\text{hex}} 10.37 \text{ \AA}$ and $c_{\text{hex}} 20.74 \text{ \AA}$.

¹ Our previous analysis for senaitite (Grey and Lloyd, 1976) covered titanium, iron, manganese, and lead only. The more comprehensive analysis given in Table 1(a) has been performed on the same sample.

TABLE 1a. Microprobe analyses (weight percent)

	<u>Crichtonite</u>	<u>Senaitite</u>
TiO ₂	60.49	58.68
Fe ₂ O ₃ *	21.14	16.20
FeO*	8.18	8.53
MnO	2.78	4.08
SrO	4.17	0.20
PbO	0.78	9.21
V ₂ O ₅	0.61	0.70
La ₂ O ₃	0.29	0.06
Ce ₂ O ₃	0.27	0.07
HfO ₂	0.23	0.13
Y ₂ O ₃	0.21	0.86
Cr ₂ O ₃	0.15	0.16
ZrO ₂	0.10	0.09
CaO	0.06	0.10
Al ₂ O ₃	0.02	0.05
ThO ₂	0.01	0.12
Nd ₂ O ₃	0.02	0.01
MgO	-	0.02
NiO	-	0.08
SiO ₂	-	-
Total	99.51	99.35

*See text for method of calculating ferrous and ferric iron. The formulae calculated from the above data and normalized to 38 oxygens are:

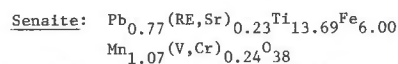
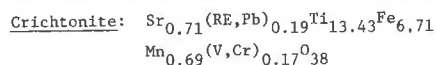


TABLE 1b. Unit-cell parameters for crichtonite, trigonal $R\bar{3}$

a_{rh}	= 9.148(2) Å	a_{hex}	= 10.374(3) Å
α_{rh}	= 69.078(6)°	c_{hex}	= 20.746(6) Å
Z_{rh}	= 1	Z_{hex}	= 3
d_{calc}	= 4.54		

For the intensity data collection, the crystal was remounted along its long dimension ($\approx a_{\text{hex}}$) on a Philips PW 1100 4-circle automatic diffractometer. Twelve high-angle reflections provided the 2θ values used to calculate the lattice parameters reported in

Table 1. Intensities were collected with graphite-monochromated $\text{MoK}\alpha$ radiation with a takeoff angle of 12.18° . A θ - 2θ scan, 3 - 22° , was used with a variable scan width given by $\Delta\theta = (1.0 + 0.3 \tan \theta)$ and a speed of $0.05^\circ \text{ sec}^{-1}$. Two background measurements, each for half the scan time, were made for each scan, one of the lower and one at the upper limit. The intensities were processed using a program written for the PW 1100 diffractometer by Hornstra and Stubbe (1972). Because of the small size ($\mu R = 0.39$) and complex shape of the crystal, an absorption correction was not applied. However, a partial compensation was achieved by averaging the intensities of equivalent reflections, $\pm (hkl, khl, lkh)$, in the rhombohedral cell. This gave an averaged unique set of 505 reflections.

Scattering factor curves for Sr, Mn, Fe, Pb, Ti, La, and O were taken from *International Tables for X-ray Crystallography III* (1962, p. 201 ff.). The curves for La, Pb, and Sr were corrected for anomalous dispersion. All computing was performed on the Monash University CDC3200 and the CSIRO CDC7600 computers.

Solution and refinement of the structure

The atom coordinates obtained for senaite in the centrosymmetric space group $R\bar{3}$ (Grey and Lloyd, 1976) were used as a starting model for crichtonite. A composite La-Pb-Sr scattering curve, consistent with the microprobe analysis, was used for the origin atom and an averaged metal scattering curve used for the other metal atom sites. Three cycles of full matrix least-squares refinement led to a conventional R value of 0.11. Both the refined isotropic temperature factors and the metal-oxygen bond lengths calculated

at this stage were consistent with an ordering of titanium, iron, and manganese atoms similar to that determined for senaite. The ordering scheme used, which is consistent with the chemical analysis, is given in Table 2. Using the corresponding separate scattering curves for each metal atom site, a further series of refinement cycles was carried out, resulting in a final R factor of 0.040 for all 505 observed data.² The final parameters are given in Table 2. Calculated bond lengths and angles are given in Table 3. Observed and calculated structure factors are listed in Table 4.

Description of the structure

Crichtonite is isostructural with senaite. Its atomic arrangement is based on a close-packed anion framework with a nine-layer stacking sequence (hhc —) in which Sr, RE, and Pb atoms occupy one of the anion sites in the cubic layers. The other metal atoms are ordered into both tetrahedral and octahedral interstices between the anion layers. Two types of metal-atom polyhedral arrangements occur, between pairs of hexagonally-stacked anion layers, and between hexagonal and cubic anion layers, h - M - h and h - M - c respectively. These are illustrated in Figures 1 and 2. Between hexagonally stacked anion layers, two types of metal atoms, $M(1)$ and $M(3)$ (Table 2), occupy octahedral sites only. The $M(3)\text{O}_6$ octahedra articulate by edge-sharing to form interconnected 12-membered hexagonal rings, with an isolated $M(1)\text{O}_6$ octahedron at the center of each ring (Fig. 1). The

² In constructing the scattering curves, the data for La were used to approximate the RE contribution and the minor elements V, Cr, Zr (0.17 atoms) were grouped with Ti.

TABLE 2. Crichtonite: final atomic coordinates and isotropic temperature factors

Atom		X	Y	Z	B (\AA^2)
M(0)	0.7 Sr + 0.2 (Pb + RE)	0.0000	0.0000	0.0000	.622(4)
M(1)	0.7 Mn + 0.3 Fe	.5000	.5000	.5000	.085(6)
M(2)	2.00 Fe	.31002(15)	.31002(15)	.31002(15)	.305(5)
M(3)	4.4 Fe + 1.6 Ti	.34821(18)	.01996(18)	.12540(18)	.303(4)
M(4)	6.00 Ti	.30861(21)	.15018(21)	.71802(21)	.388(4)
M(5)	6.00 Ti	.47337(20)	.64054(21)	.08370(20)	.334(4)
O(1)	6.00 O	.30300(77)	.37824(77)	.62878(77)	1.00 (1)
O(2)	6.00 O	.15029(76)	.93711(75)	.23654(75)	.88 (1)
O(3)	6.00 O	.91852(73)	.30110(72)	.45916(73)	.63 (1)
O(4)	6.00 O	.14475(75)	.98866(74)	.51544(74)	.75 (1)
O(5)	6.00 O	.39014(73)	.13445(75)	.48615(74)	.64 (1)
O(6)	6.00 O	.70853(72)	.07152(74)	.24216(73)	.61 (1)
O(7)	2.00 O	.21402(50)	.21402(50)	.21402(50)	.71 (2)

h-M-c metal-atom layers, two per unit cell, contain metals in both octahedral and tetrahedral sites. The octahedrally-coordinated atoms, *M(4)* and *M(5)*, join by edge-sharing into six-membered hexagonal rings which are interlinked via corner-sharing with the basal oxygens of the *M(2)O₄* tetrahedra (Fig. 2).

The cubic-stacked anion layers have strontium/lead cations ordered into one of the available 13 anion sites per unit cell, and this is shown as a filled circle in Figure 2.

The linking of polyhedra between layers is illustrated in Figures 3 and 4. In Figure 3 the arrangement

TABLE 3. Crichtonite—interatomic distances (Å) and angles (degrees)

<u>M(1) octahedron</u>			<u>M(2) tetrahedron</u>			<u>Sr Site</u>					
	Distance	O-M-O angle		Distance	O-M-O angle		Distance	O-M-O angle			
M(1) - O(1)	[6]	2.205*	M(2) - O(5)	[3]	1.966	Sr - O(2)	[6]	2.753			
			- O(7)		1.991	- O(6)	[6]	2.831			
O(1) - O(1) ¹	[6]	3.07	88.11*	O(5) - O(5) ¹	[3]	3.27	112.27	O(2) - O(6)	[6]	2.73	58.52
- O(1) ¹¹	[6]	3.17	91.89	- O(7)	[3]	3.17	106.51	O(2) - O(2)	[6]	2.77	60.41
								O(6) - O(6)	[6]	2.84	60.29
								O(2) - O(6) ¹	[6]	2.85	61.35
<u>M(3) octahedron</u>			<u>M(4) octahedron</u>			<u>M(5) octahedron</u>					
M(3) - O(4)	1.940		M(4) - O(2)	1.873		M(5) - O(1)	1.860				
- O(3)	1.976		- O(1)	1.937		- O(4)	1.864				
- O(2)	1.999		- O(2)	1.949		- O(3)	1.930				
- O(4) ¹	2.017		- O(6)	1.982		- O(5)	2.000				
- O(7)	2.019		- O(5)	2.023		- O(6)	2.013				
- O(2) ¹	2.086		- O(6) ¹	2.050		- O(5) ¹	2.136				
O(4) - O(4) ¹	2.69	85.59	O(1) - O(6)	2.59	80.85	O(5) - O(5) ¹	2.56	76.35			
- O(2)	2.73	83.57	O(5) - O(3)	2.59	81.21	- O(3)	2.59	78.82			
O(7) - O(2)	2.72	82.92	- O(6)	2.61	81.33	O(6) - O(1)	2.59	83.72			
- O(2) ¹	2.72	85.14	- O(1)	2.72	86.55	- O(5)	2.61	81.14			
O(2) - O(4) ¹	2.77	85.36	O(2) - O(6)	2.73	88.10	O(1) - O(5)	2.81	89.09			
O(4) - O(7)	2.81	88.12	O(1) - O(3)	2.84	93.76	O(4) - O(6)	2.78	91.67			
- O(3)	2.82	92.32	O(6) - O(6) ¹	2.84	89.68	O(3) - O(5) ¹	2.81	91.31			
- O(2) ¹	2.88	91.39	O(2) - O(1)	2.85	96.99	- O(4)	2.84	97.01			
O(4) - O(3)	2.86	91.67	- O(3)	2.88	97.77	O(1) - O(4)	2.83	98.79			
O(3) - O(7)	2.89	92.87	- O(6)	2.85	95.31	- O(3)	2.92	101.33			
- O(2)	3.02	98.95	O(6) ¹ - O(3)	2.88	94.39	O(5) ¹ - O(4)	2.89	96.73			
O(4) ¹ - O(2) ¹	3.02	100.11	- O(5)	2.96	93.22	- O(6)	2.98	91.73			
<u>Metal-Metal distances**</u>											
M(1) - M(5)	c	3.627	M(2) - M(5)	c	3.389	Sr - M(4)	c	3.398			
- M(4)	c	3.773	- M(4)	c	3.487						
			- M(3)	c	3.483						
M(3) - M(3) ¹	e	2.904	M(4) - M(5)	e	2.946	M(5) - M(5)	e	3.252			
- M(3) ¹¹	e	3.011	- M(5) ¹	e	3.041						
- M(5)	c	3.361	M(4) ¹ - M(5)	e	3.066						
- M(4)	c	3.530									
- M(5) ¹	c	3.478									
- M(4) ¹	c	3.594									
- M(5) ¹¹	c	3.622									
- M(4) ¹¹	c	3.718									

*Standard deviations for M-M, M-O and O-O are 0.003, 0.007 and 0.010 Å respectively and for angle O-M-O 0.3 degrees.

**c and e refer to corner- and edge-shared linkages.

of octahedra for three consecutive metal-atom layers is shown. Between adjacent h-M-c and h-M-h layers, the 6-membered and 12-membered rings are arranged concentrically about the isolated M(1)O6 octahedra and interlink by corner-sharing only. Between pairs of h-M-c layers, the 6-membered rings share three octahedral edges with each of three other

units. The tetrahedra-to-octahedra linkages between layers are shown in Figure 4. The basal oxygens of the M(2)O4 tetrahedron form the corner-shared linkages of M(2) to atoms M(3) and M(4) in the 6-membered rings and the apical oxygen corner-links M(2) to the three M(1) atoms in each trigonal triplet, which is the basic building unit in the h-M-h layers.

TABLE 4. Observed and calculated structure factors for crichtonite

Table with multiple columns for H, K, L, FO, FC and corresponding values for observed and calculated structure factors.

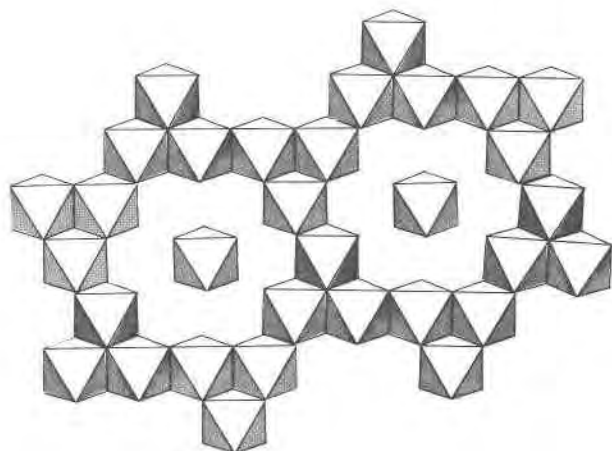


FIG. 1. Polyhedral representation of the metal atom $M(1)$, $M(3)$ arrangement between pairs of hexagonal stacked anion layers, viewed approximately along $(001)_{\text{hex}}$.

Interatomic distances

Polyhedral bond lengths and angles for crichtonite are given in Table 3, and in Table 5 the mean bond lengths are compared with the corresponding values for the isostructural mineral senaite.

The strontium-rich site in the cubic-stacked anion layers is bonded to six oxygens within the layer at a separation of 2.83 Å and to three oxygens in both adjacent layers at the somewhat shorter distance of 2.75 Å, resulting in twelve-coordination. The average of these two, 2.79 Å, is close to the value calculated from the ionic radii, $[\text{Sr}_{0.71}(\text{RE}, \text{Pb})_{0.19}]-\text{O} = 2.78$ Å (Shannon and Prewitt, 1969). Crichtonite shows the same ordering of metal ions as does senaite, *i.e.* tet-

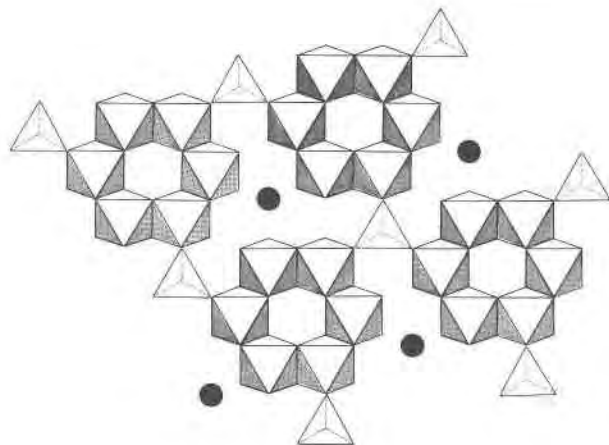


FIG. 2. Polyhedral representation of the metal atom $M(2)$, $M(4)$, $M(5)$ arrangement between hexagonal- and cubic-stacked anion layers, viewed along $(001)_{\text{hex}}$. The filled circles represent strontium.

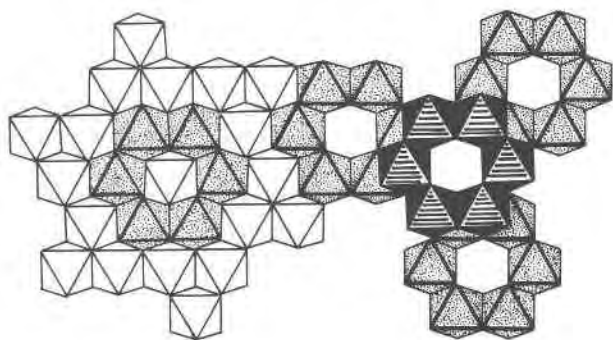


FIG. 3. Polyhedral representation of sections corresponding to three consecutive metal atom layers, showing interlayer articulation of octahedra. Tetrahedra not shown.

ravalent titanium ions are ordered into octahedral sites $M(4)$ and $M(5)$ in the h - M - c layers, with the remaining small cations, Ti^{4+} and Fe^{3+} , going into the $M(3)$ octahedra forming the 12-membered rings in the h - M - h layers. The mean $M(3)-$, $M(4)-$, and $M(5)-\text{O}$ distances for senaite and crichtonite are identical within experimental error. The two structures differ only in the nature of the larger cations, $M(1)$ and $M(2)$, which lie along the trigonal axes. These ions are colinear with the large divalent ions, RE^{3+} , Pb^{2+} , Sr^{2+} , in the anion framework, and their ordering appears to be dependent on the size of the latter. Thus in crichtonite, which has mainly the smaller Sr^{2+} ion in the anion framework, the mean $M(1)-\text{O}$ and $M(2)-\text{O}$ distances are shorter than the corresponding values for senaite, with larger Pb^{2+} ions in the cubic-stacked anion layers. Whereas in senaite the isolated octahedral site $M(1)$ in the h - M - h layer is fully occupied by manganese, the crichtonite unit cell composition contains only 0.7 atom of manganese, which orders into this site. The observed reduction in the $M(1)-\text{O}$ bond length from senaite to crichtonite is consistent with the remainder of this site being occupied by Fe^{2+} . Also, whereas in senaite the tetrahedral site $M(2)$ is fully occupied by Fe^{2+} , in crichtonite the reduced $M(2)-\text{O}$ bond length may be explained by the introduction of some ferric iron into this site, $(\text{Fe}_{0.7}^{2+} \cdot \text{Fe}_{0.3}^{3+})-\text{O} = 1.97$ Å (Shannon and Prewitt, 1969). An interesting feature of the crichtonite structure is the extremes shown in the polyhedral distortions between polyhedra located on the trigonal axes and those around it. Thus, whereas the $M(1)\text{O}_6$ octahedron is almost perfect, with equal $M-\text{O}$ bond lengths and $\text{O}-M-\text{O}$ angles deviating by less than 2 degrees from ideal values, the $M(5)-\text{O}_6$ octahedron is greatly distorted with $\Delta M(1)-\text{O} = 0.28$ and $\Delta \text{O}-M-\text{O} = 25^\circ$. $M(3)-\text{O}_6$ and $M(4)-\text{O}_6$ octahedra

are somewhat less distorted than $M(5)-O_6$, and the relative distortions may be qualitatively explained in terms of the varying amounts of edge- and corner-sharing between polyhedra. Thus, the polyhedra about $M(1)$ and $M(2)$ centered on the trigonal axes have *only* corner-shared linkages, whereas $M(3)O_6$ and $M(4)O_6$ octahedra each share edges with three other octahedra, and $M(5)-O_6$ has distortions resulting from cation-cation repulsions across *four* octahedral edges.

The composition of crichtonite and related minerals

Sr, Pb, and RE occupy only one of the available 39 anion sites in the unit cell, leaving 38 oxygen sites, and so the unit cell formula is normalized to 38 O. Expressed in this way the formula is $Sr_{0.71}(RE,Pb)_{0.19}Ti_{13.43}Fe_{6.71}Mn_{0.69}(V,Cr)_{0.17}O_{38}$. By comparison the formula for senaite is $Pb_{0.77}(RE,Sr)_{0.23}Ti_{13.69}Fe_{6.00}Mn_{1.07}(V,Cr)_{0.24}O_{38}$. Both of these minerals may be considered as members of a general solid solution series involving replacement of lead by strontium, *i.e.* $(RE,Pb,Sr)_{1-x}M_{21}O_{38}$, when M is largely Ti^{4+} , Mn^{2+} , Fe^{3+} , Fe^{2+} , and the variable x indicates that full occupation of the anion site by large cations is not always achieved. In view of the interchangeability of Pb^{2+} and Sr^{2+} we suggest that the mineral names senaite and crichtonite be assigned to the end-member phases containing either dominant lead or dominant strontium respectively.

Apart from the present work the only reported quantitative analysis for crichtonite is that by Hey *et al.* (1969), who analyzed for ferric oxide, ferrous oxide, and titanium oxide and obtained a total of 94.84 percent. On the basis that the deficit is made up by strontium oxide, their calculated composition normalized to 38 oxygens is $Sr_{0.87}Ti_{14.46}Fe_{3.13}^{3+}Fe_{3.54}^{2+}O_{38}$, *i.e.* it conforms closely to the general formula Sr_{1-x}

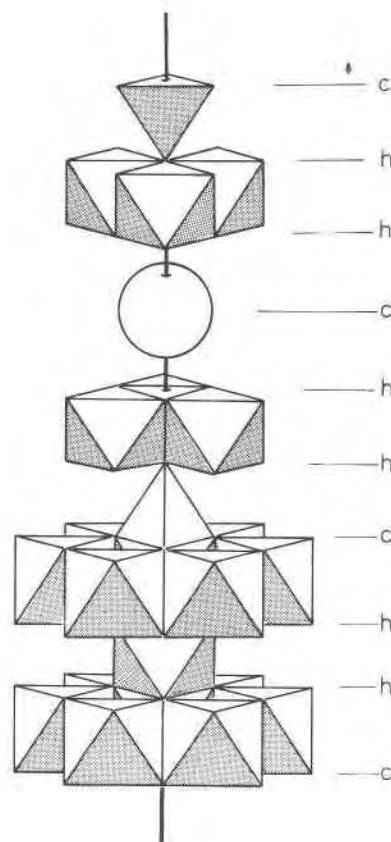


FIG. 4. Arrangement of octahedra and tetrahedra along the trigonal axis for crichtonite. The circle represents strontium. The anion layer stacking sequence is shown.

$M_{21}O_{38}$ (actually $Sr_{1-x}M_{21.12}O_{38}$), with a value of x , 0.13, quite close to our values for both crichtonite and senaite. The calculated density based on this formation is 4.49 g cm^{-3} , which agrees with the observed value 4.46 ± 0.04 (Hey *et al.*, 1969).

TABLE 5. Comparison of mean bond lengths for crichtonite and senaite (Grey and Lloyd, 1976)

	CRICHTONITE		SENAITE	
	Site Occupancy	Mean M-O (Å)	Site Occupancy	Mean M-O (Å)
M(0)	0.71 Sr + 0.19 (Pb + RE)	2.792 (7)	0.83 Pb	2.817 (17)
M(1)	0.7 Mn + 0.3 Fe^{2+}	2.205 (7)	Mn	2.227 (17)
M(2)	1.4 Fe^{2+} + 0.6 Fe^{3+}	1.972 (7)	2 Fe^{2+}	1.996 (18)
M(3)	4.4 Fe^{3+} + 1.6 Ti	2.006 (7)	4.3 Fe^{3+} + 1.7 Ti^{4+}	1.998 (18)
M(4)	6 Ti	1.969 (7)	6 Ti	1.976 (18)
M(5)	6 Ti	1.967 (7)	6 Ti	1.964 (18)

The first reported analysis for senaite, by Hussak and Prior (1898), gives a composition $\text{Pb}_{0.89}\text{Ti}_{13.48}\text{Fe}_{1.08}^{2+}\text{Fe}_{4.76}^{3+}\text{Mn}_{1.86}^{2+}\text{Mg}_{0.23}\text{O}_{38.18}$ which when normalized to 38 oxygens approximates the general formula given above, although the number of metals, M , is somewhat greater than 21 at $\text{Pb}_{1-x}\text{M}_{21.32}\text{O}_{38}$, $x = 0.12$. Subsequent analyses were reported by Hussak and Reitinger (1903) and Freise (1930) on material in which all the iron was reported in the ferrous state. The unit cell contents have been calculated for each of these analyses by Rouse and Peacor (1968). The results are all very similar and give an average formula $\text{Pb}_{0.99}\text{Ti}_{13.02}\text{Fe}_{7.07}^{2+}\text{Mn}_{3.84}\text{Zr}_{0.09}\text{Mg}_{0.05}\text{O}_{38.17}$ which is normalized to $\text{Pb M}_{24}\text{O}_{38}$, *i.e.* the pure ferrous senaite contains three more metal atoms per unit cell than found from our structure analyses for senaite with predominantly ferric iron and for crichtonite. A very reasonable model for senaite (Fe^{2+}) may be constructed in the noncentric space group $R3$ by incorporation of the extra metals into the three-fold site 3(b) in the $h-M-h$ layers. This is discussed in the next section.

The mineral davidite is almost certainly isostructural with senaite and crichtonite. Although a structure analysis has not been reported, it has a very similar powder pattern to that for senaite (Rouse and Peacor, 1968), and single-crystal patterns display the same symmetry, space-group requirements and lattice parameters (Pabst, 1961). The natural mineral is metamict but may be recrystallized by heating in air at temperatures above 700°C (Pabst, 1961). The published crystallographic data for davidite thus would apply to material in which all iron was in the ferric state. Pabst (1961) has reported full chemical analyses for davidites from three different countries. The averaged unit-cell formula obtained from these data is $(\text{RE,U})_{1.51}(\text{Ti,V,Cr,Mg,Fe,Al})_{19.35}\text{O}_{38.00}$, with iron in both ferrous and ferric states. For the reconstituted mineral containing only ferric iron, the formula becomes $(\text{RE,U})_{1.51}(\text{Ti,V,Cr,Mg,Fe,Al})_{19.35}\text{O}_{37.66}$, or expressed in terms of 38 oxygens $(\text{Pb,RE,U})_{1.52}\text{M}_{19.52}\text{O}_{38}$. This differs from the general formula for senaite and crichtonite in having more than one atom per unit cell of large cations, in this case predominantly rare earths and uranium, and at the same time less than 21 small-cation sites. Rare earths and uranium are considerably smaller than Pb^{2+} and Sr^{2+} , and it is likely that the extra 0.5 atoms per unit cell occupy octahedral sites, particularly site $M(1)$. We are presently carrying out a single-crystal structure analysis on a recrystallized davidite which should throw some light on these interesting features.

Structural relationships to other close-packed minerals

Crichtonite, senaite, and davidite are all found in intimate intergrowth or otherwise close association with ilmenite, and several researchers (Hussak and Reitinger, 1903; Shawe, 1953; Pabst, 1961) considered them to have structures closely related to that of the latter. However, our structure analyses for both senaite (Grey and Lloyd, 1976) and crichtonite show no obvious structural relationships with ilmenite. In ilmenite the oxygens form a hexagonal close-packed array, and two-thirds of the available octahedral sites between pairs of close-packed anion layers are alternately occupied by all titanium or all iron atoms respectively (Barth and Posnjak, 1934). Across the anion layers iron-titanium octahedra share faces, and within layers the metal octahedra articulate by edge-sharing into the honeycomb pattern shown in Figure 5(a). By contrast, in crichtonite and senaite there is no face-sharing of octahedra across close-packed layers and the articulation of octahedra within layers is quite different from that in ilmenite. However, as discussed above, reported analyses for senaite containing only ferrous iron are consistent with a formulation $\text{PbM}_{24}\text{O}_{38}$, containing three more metal atoms than found for senaite (Fe^{3+}) and crichtonite. A very reasonable structural model may be postulated for senaite (Fe^{2+}) which does in this instance contain elements of the ilmenite structure. The proposed structure is shown in Figure 5(b). It is basically the same as found for crichtonite, but has the three extra metal atoms ordered into the $h-M-h$ layer. This structure is necessarily noncentric, space group $R3$. The resulting honeycomb network of octahedra in the $h-M-h$ layer, and the sharing of octahedral faces across the hexagonal anion layers is the same as in ilmenite [compare Fig. 5(a)]. Also, as titanium atoms have been found to order into the $c-M-h$ layers, and the extra metals (Fe^{2+} and Mn^{2+}) must order into the $h-M-h$ layers, then the face-sharing will be between Fe/Mn and Ti pairs, as in ilmenite (FeTiO_3)-pyrophanite (MnTiO_3) (Posnjak and Barth, 1934). It is tempting to suggest that the structure shown in Figure 5(b) is the original basic structure for senaite and related minerals, containing only ferrous iron, $\text{AM}_{24}\text{O}_{38}$, and that the $\text{AM}_{21}\text{O}_{38}$ structures are ordered intermediates derived from natural oxidation and leaching of iron (and manganese), *i.e.* analogous to the formation of the ordered intermediate phase pseudorutile, $\text{Fe}_2^{3+}\text{Ti}_3\text{O}_9$, in the natural alteration of ilmenite, $\text{Fe}^{2+}\text{TiO}_3$ (Grey and Reid, 1975).

Rouse and Peacor (1968) predicted a close rela-

relationship between the structures of senaite and magnetoplumbite, $\text{PbFe}_{12}\text{O}_{19}$ (Berry, 1951). Certainly the latter mineral has the common feature of large cations occupying anion sites in a close-packed anion framework. However, the stacking sequence in magnetoplumbite is quite different (*cchhh*...), and the polyhedral articulations have no obvious relationship to those in senaite and crichtonite. In particular, the cubic close-packed layers in magnetoplumbite have the spinel structure, while, between cubic and hexagonal layers, octahedra share faces. Also, the lead atoms occupy sites in *hexagonally* stacked anion layers in magnetoplumbite.

Although the crichtonite, senaite, davidite minerals appear to have no obvious gross structural relation-

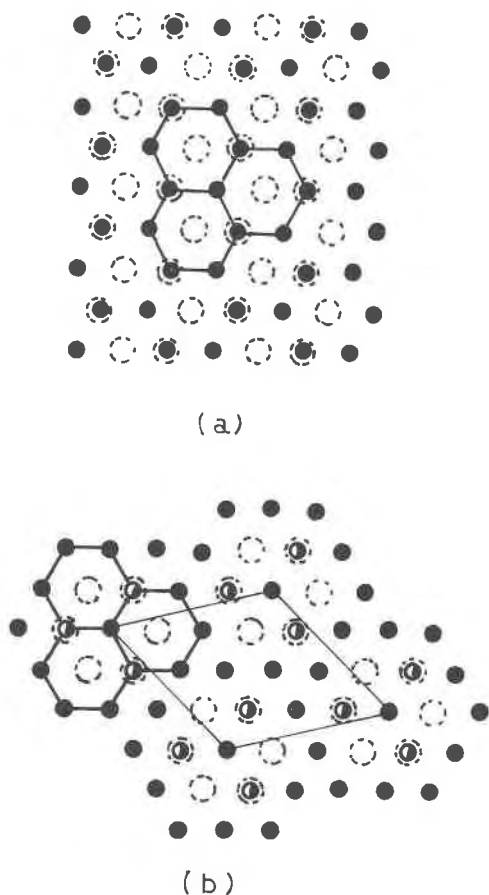


FIG. 5. Metal atom arrangement across a hexagonally stacked anion layer (a) in ilmenite, (b) in proposed structure for senaite (Fe^{2+}), $\text{PbM}_{24}\text{O}_{38}$. Metals at the two levels shown by full and dashed circles. Half filled circles in (b) represent extra metals incorporated into the senaite structure. Rhombohedral unit cell for senaite/crichtonite shown in (b). Oxygens not shown.

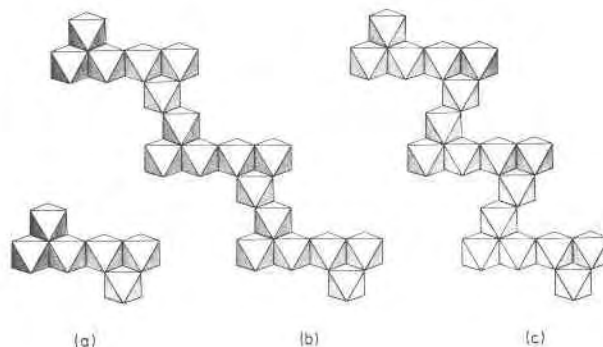


FIG. 6. (a) Basic structure building unit, for (b) crichtonite (*h-M-h* layers) and (c) norbergite.

ships with other close-packed mineral structures, they do have structural elements in common. In particular, the essential building unit in the *h-M-h* layers, a pair of trigonal triads of edge-shared octahedra, is also the essential structural element in the hexagonally close-packed humite mineral, norbergite (Gibbs and Ribbe, 1969). In both cases the 6-octahedra units link into infinite chains by further edge-sharing, although the shared edges are different, as shown in Figure 6. Whereas in norbergite the chains are cross-linked by tetrahedra, in crichtonite the chains link together by edge-sharing as shown in Figure 1. Also, in common with a large number of close-packed silicate and oxide minerals such as olivines, pyroxenes, spinels and humites, the oxygen at the intersection of the three shared octahedral edges of each trigonal triad forms the vertex of an occupied tetrahedral site (Fig. 4).

Across a hexagonal anion layer in crichtonite the occupied octahedral sites are mutually exclusive, *i.e.* the double layer of octahedra has stoichiometry MO_2 and forms the basis for yet another interesting hexagonal close-packed two-layer structure type, typical examples of which are olivines (Birle *et al.*, 1968) and humites (Gibbs and Ribbe, 1969). In this hypothetical structure, the anion site occupied by Sr in crichtonite would contain oxygen, which would form the vertex of a second occupied tetrahedral site per unit cell, giving a formula $\text{M}_{13}^{\text{oct}}\text{M}_2^{\text{tet}}\text{O}_{26}$. In further work on these structures we hope to synthesize such a compound, and also are working on the structure solution for davidite.

Acknowledgments

The authors wish to thank the Smithsonian Institution for kindly providing the samples of senaite and crichtonite, and Drs. J. Campbell and P. Kelly of the Melbourne University Geology Department for carrying out the microprobe analysis. The authors

also wish to thank Dr B. M. Gatehouse of Monash University for kindly permitting use of equipment supported by funds from the Australian Research Grants Committee.

References

- BARTH, T. F. W. AND E. POSNJAK (1934) The crystal structure of ilmenite. *Z. Kristallogr.* **88**, 265.
- BERRY, L. G. (1951) The unit cell of magnetoplumbite. *Am. Mineral.* **36**, 512-514.
- BIRLE, J. D., G. V. GIBBS, P. B. MOORE AND J. V. SMITH (1968) Crystal structures of natural olivines. *Am. Mineral.* **53**, 807-824.
- FREISE, F. W. (1930) Der Mineralbestand der Konglomerate von Diamantina, Staat Minas Geraes, Brasilien. *Chem. Erde*, **6**, 66-71.
- GREY, I. E. AND D. J. LLOYD (1976) The crystal structure of senaite. *Acta Crystallogr.* **B32**, 1509-1513.
- AND A. F. REID (1975) The structure of pseudorutile and its role in the natural alteration of ilmenite. *Am. Mineral.* **60**, 898-906.
- GIBBS, G. V. AND P. H. RIBBE (1969) The crystal structures of the humite minerals: I. Norbergite. *Am. Mineral.* **54**, 376-390.
- HEY, M. H., P. G. EMBREY AND E. E. FEJER (1969) Crichtonite, a distinct species. *Mineral. Mag.* **37**, 349-355.
- HORNSTRA, J. AND B. STUBBE (1972) *PW 1100 Data Processing Program*, Philips Research Labs, Eindhoven.
- HUSSAK, E. AND G. T. PRIOR (1898) On senaite, a new mineral belonging to the ilmenite group, from Brazil. *Mineral. Mag.* **12**, 30-32.
- AND J. REITINGER (1903) Ueber Monazit, Xenotim, Senait und natürliches Zirconoxyd aus Brasilien. *Z. Kristallogr.* **37**, 550-579.
- PABST, A. (1961) X-ray crystallography of davidite. *Am. Mineral.* **46**, 700-718.
- POSNJAK, E. AND T. F. W. BARTH (1934) Notes on some structures of the ilmenite type. *Z. Kristallogr.* **88**, 271-280.
- ROUSE, R. C. AND D. R. PEACOR (1968) The relationship between senaite, magnetoplumbite and davidite. *Am. Mineral.* **53**, 869-879.
- SHANNON, R. D. AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, **B25**, 925-946.
- SHAW, D. R. (1953) *Heavy detrital minerals in stream sands of the eastern Sierra Nevada between Leevining and Independence, California*. Ph.D. Dissertation, Stanford University, 190 p. [Abstracted in *Dissertation Abstracts*, **XIV**, 369-370, (1954)].
- STRUNZ, H. (1970) *Mineralogische Tabellen*. Fifth Edition Akademische Verlagsgesellschaft, Leipzig. 621 p.

Manuscript received, February 17, 1976; accepted for publication, July 20, 1976.